Chlorine Isotopic Exchange between Lithium Chloride-36 and Some Compounds containing Two Non-equivalent Exchangeable Chlorine Atoms

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Rate constants have been determined for the chlorine-isotopic exchange reactions in sulpholane solution between lithium chloride-36 and compounds containing two non-equivalent exchangeable chlorine substituents, *viz.* 2,5-dichloro-3-nitrothiophene, 1,3-dichloro-2,4-dinitrobenzene, and 4-chloro-3,5-dinitrobenzenesulphonyl chloride.

Chlorine-isotopic exchange reactions between lithium chloride and activated aromatic chloro-compounds, which follow simple exchange kinetics, have been studied extensively.[1-5] For one case where two non-equivalent activated chlorine substituents were present in the aromatic molecule, *viz.* for 1,3-dichloro-2,4-dinitrobenzene (I), straightforward simple kinetics were nevertheless obtained.[3] This result suggested that, under the experimental conditions employed, only one chlorine atom in the organic molecule underwent a similar rate of exchange. One example of complex exchange (defined as one in which at least one reactant has two or more exchangeable atoms that are chemically not equivalent [6]) has been reported, in which three simultaneous reactions take place.[4] We now report on several cases in which two simultaneous reactions take place.

Method.—Experimentally one measures the fraction (F) of exchange as a function of time (t). As for cases of simple exchange a semilogarithmic plot of $(1 - F)$ *versus* t is then constructed. For cases of complex exchange one observes an initial curve (*a*), proceeding to a straight line at higher t values. A typical experimental plot is shown in Figure 1. The straight line portion of the overall reaction can be extrapolated to zero t. The slope of this line (*b*), representing the slower component of the complex reaction, determines the time required for half-exchange $(t_{\frac{1}{2}})_B$, and this leads to an estimate of rate $(R)_B$ and hence of rate constant $(k_2)_B$.[1] Subsequent subtraction of the straight line portions of the plot from the overall curve then leads to a second straight line (*c*), representing the fast component reaction of the complex process. Again, the slope of this line affords rate $(R)_C$ and rate constant $(k_2)_C$. The direct graphical procedure is usually satisfactory, but a more objective method was here preferred, involving least-squares analysis of the data,[4] based on principles discussed by Cumming.[7]

The two intercepts of these straight line plots, for zero t, which are obtained essentially independently of each other, add up to values very close to the theoretical value of unity. This provides an independent check on whether the system is 'well behaved' or not. Intercepts of 0.5 for t_0 apply only for limiting experimental circumstances,[6] which do not obtain here.

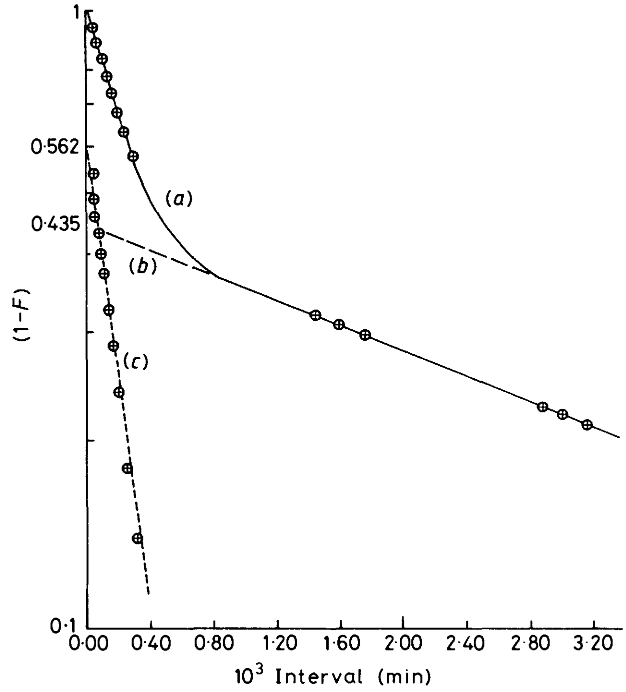


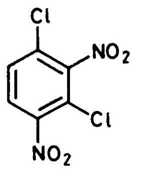
Figure 1. Complex exchange curve for the reaction of 2,5-dichloro-3-nitrothiophene with lithium chloride-36 in sulpholane solution at 362.9 K. Solid curve: (*a*), complex exchange curve (experimental); broken curves: (*b*), exchange of chlorine at the 5-position, (*c*), exchange of chlorine at the 2-position

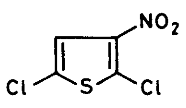
2,5-*Dichloro*-3-*nitrothiophene*.—Compound (II) possesses two activated non-equivalent chlorine substituents. A typical plot, for a reaction carried out in sulpholane solution, is given in Figure 1, where it is shown that rate constants can readily be derived graphically for the two component reactions. The accuracy of the fit between the experimental values of $(1 - F)$, and those recalculated from the (least-squares) computed rate constants, can be assessed from the data given in Table 1, for a reaction followed up to 78% exchange.

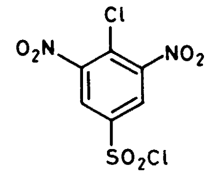
The component rate constants calculated for the two thienyl positions and derived activation parameters are given in Tables 2 and 3, respectively. In view of the less than straightforward method required for these calculations, the degree of precision obtained can be regarded as satisfactory. The rate data by themselves do not allow a conclusion to be reached as to which chlorine position undergoes the slower, and which the faster, reaction.

1,3-*Dichloro*-2,4-*dinitrobenzene*.—Previous work,[3] referred to above, on the chlorine isotopic exchange with the title compound (I), carried out in dimethyl sulphoxide solution, appeared to follow simple reaction kinetics, in the range 354—375 K.

We have now observed complex exchange for this compound in sulpholane solution in the temperature range 395—427 K (Tables 4 and 5). The temperature range over which both component reactions could be determined together was fairly narrow, and this contributes to the poor precision with which the activation parameters for the reaction at the 1-position could be determined. Better precision of the parameters for the reaction at the 3-position was attainable by including a rate constant determined beyond the range of the complex reaction as normally recognised (*cf.* Figure 1). At 426.9 K the fast reaction is virtually complete after 30 min, and the exchange curve is then seen as a straight line *not* passing through unity on extrapolation to t_0 (Figure 2).


(I)


(II)


(III)

In our earlier work [3] it was argued that the faster reaction for compound (I) involved chlorine exchange at the 1-position, and this interpretation is believed to remain valid.

Table 1. Comparison of experimental and calculated results for the reaction of 2,5-dichloro-3-nitrothiophene with lithium chloride-36 in sulpholane solution at 362.9 K

[Org] 0.014 67 mol dm^{-3} [LiCl] 0.014 80 mol dm^{-3}

X_0 8 356 counts min^{-1} X_∞ 2 830 counts min^{-1}

Time (min)	Corrected count rate (X_t) (min^{-1}) [a]	$(1 - F)_{obs.}$	$(1 - F)_{calc.}$ [b]
15.0	8 153	0.9584	0.9593
30.0	7 952	0.9221	0.9237
45.0	7 764	0.8880	0.8905
60.0	7 603	0.8589	0.8596
75.0	7 455	0.8321	0.8308
90.0	7 308	0.8055	0.8039
120	7 029	0.7550	0.7555
150	6 813	0.7159	0.7134
180	6 604	0.6781	0.6769
240	6 266	0.6170	0.6176
300	6 019	0.5723	0.5729
1 470	4 592	0.3187	0.3200
1 620	4 542	0.3098	0.3101
1 800	4 491	0.3006	0.2986
2 910	4 129	0.2351	0.2368
3 030	4 110	0.2316	0.2309
3 180	4 069	0.2242	0.2238

[a] Corrected for chemical yield. [b] Mean deviation 0.25%.

4-*Chloro*-3,5-*dinitrobenzenesulphonyl Chloride*.—Complex exchange kinetics were also recorded for compound (III), in which an activated aromatic chlorine and a chlorine on a sulphonyl side chain [8] may undergo exchange simultaneously with $^{36}Cl^-$. The slower rate of exchange could be readily measured, and reasonably precise activation parameters derived (Table 6). For the fast exchange process, however, only approximate rate constants could be obtained, from the few available data points, since in the temperature range 305—311 K we were dealing with reaction half-times of *ca.* 15 s, and 305 K is at the lower limit for possible kinetic measurements in sulpholane solution.

For this system it was simple to identify the two component reactions: the slow reaction proceeded at a rate close to that predicted from a published σ-constant of the *p*-SO_2Cl substituent in reactions observed for a series of 1-chloro-2,6-dinitrobenzenes,[9] and the fast reaction at the SO_2Cl group was that expected from available data for other benzenesulphonyl chlorides, *e.g.* the rate constant for chlorine isotopic exchange

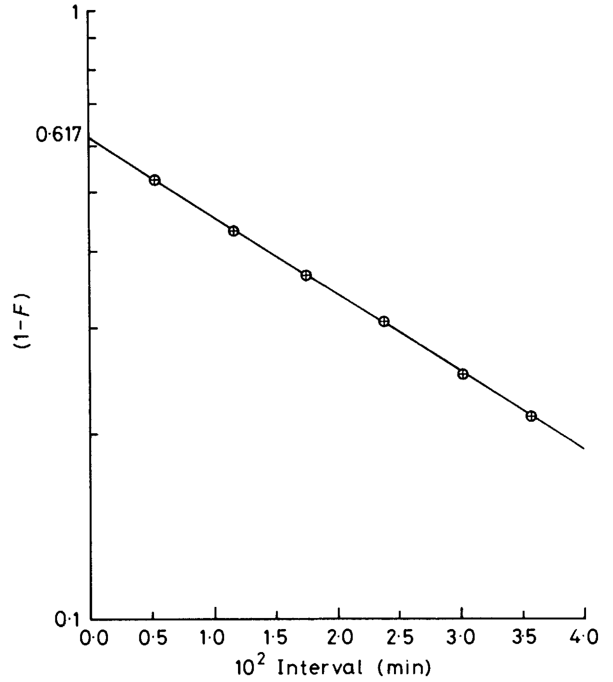


Figure 2. Complex exchange curve for the reaction of 1,3-dichloro-2,4-dinitrobenzene with lithium chloride-36 in sulpholane solution at 426.9 K. Circles: experimental points

Table 2. Exchange reaction between 2,5-dichloro-3-nitrothiophene (0.0142—0.0147 mol dm^{-3}) and lithium chloride-36 (0.0148 mol dm^{-3}) in sulpholane solution

	Fast component reaction [a]			Slow component reaction [a]		
Temp. (K)	$(t_{\frac{1}{2}})_C$ (min)	$10^3 (k_2)_C$ (dm^3 mol^{-1} s^{-1})	Intercept, $(1 - F)_c$	$(t_{\frac{1}{2}})_B$ (min)	$10^4 (k_2)_B$ (dm^3 mol^{-1} s^{-1})	Intercept, $(1 - F)_b$
362.9	135.3 ± 0.75	3.76 ± 0.020	0.562	3 650 ± 140	1.68 ± 0.065	0.435
369.1	94.4 ± 2.0	5.75 ± 0.12	0.521	2 320 ± 330	2.58 ± 0.34	0.454
375.6	64.2 ± 2.0	9.52 ± 0.30	0.443	1 140 ± 22	4.58 ± 0.090	0.552
386.6	28.6 ± 2.2	22.4 ± 0.16	0.409	344 ± 6.9	14.4 ± 0.28	0.589
393.1	18.51 ± 0.91	37.0 ± 1.8	0.383	199 ± 8.8	25.1 ± 1.1	0.600

[a] ± refers to standard deviations.

Table 3. Activation parameters[a] for the component exchange reactions between 2,5-dichloro-3-nitrothiophene and lithium chloride-36 in sulpholane solution

Parameter	Fast component reaction[b]	Slow component reaction[b]
$\Delta H^‡$/kJ mol^{-1}	87.6 ± 3.3	106.3 ± 7.8
$\Delta S^‡$/J K^{-1} mol^{-1}	−51.9 ± 8.8	−27 ± 21
$\Delta G^‡$/kJ mol^{-1}	105.7 ± 6.4	115.6 ± 15
r	0.999	0.997

[a] At 348.1 K. [b] ± refers to standard deviations.

Table 4. Exchange reaction between 1,3-dichloro-2,4-dinitrobenzene (0.0127—0.0144 mol dm^{-3}) and lithium chloride-36 (0.0152—0.171 mol dm^{-3}) in sulpholane solution

	Reaction at the 1-position[a]			Reaction at the 3-position[a]		
Temp. (K)	$(t_{\frac{1}{2}})_C$ (min)	$10^3\,(k_2)_C$ (dm^3 mol^{-1} s^{-1})	Intercept, $(1-F)_c$	$(t_{\frac{1}{2}})_B$ (min)	$10^4\,(k_2)_B$ (dm^3 mol^{-1} s^{-1})	Intercept, $(1-F)_b$
394.9	240 ± 12	3.30 ± 0.17	0.336	1 980 ± 31	2.44 ± 0.038	0.670
403.3	131 ± 5.5	6.04 ± 0.025	0.338	1 190 ± 52	4.26 ± 0.19	0.640
412.9	68.0 ± 1.6	10.5 ± 0.33	0.341	487 ± 11	9.23 ± 0.40	0.659
426.9				203 ± 2.8	25.5 ± 0.31	0.617

[a] ± refers to standard deviations.

Table 5. Activation parameters[a] for the component exchange reactions between 1,3-dichloro-2,4-dinitrobenzene and lithium chloride-36 in sulpholane solution

Parameter	Reaction at the 1-position[b]	Reaction at the 3-position[b]
$\Delta H^‡$/kJ mol^{-1}	84.5 ± 27	100.9 ± 6.8
$\Delta S^‡$/J K^{-1} mol^{-1}	−81 ± 67	−61 ± 17
$\Delta G^‡$/kJ mol^{-1}	112.6 ± 51	122.2 ± 13
r	0.999	0.999

[a] At 348.1 K. [b] ± refers to standard deviations.

Table 6. Exchange reaction between 4-chloro-3,5-dinitrobenzenesulphonyl chloride (0.0140—0.0158 mol dm^{-3}) and lithium chloride-36 (0.0145—0.0197 mol dm^{-3}) in sulpholane solution

Temp. (K)	Reaction at sulphur $(k_2)_C$ (dm^3 mol^{-1} s^{-1})[a]	Reaction at the 4-position $10^2(k_2)_B$ (dm^3 mol^{-1} s^{-1})[b,c]
305.3	~5.7	1.04 ± 0.040
308.3	~6.0	1.25 ± 0.18
311.0	~6.7	1.78 ± 0.083
318.0		3.08 ± 0.20
323.1		4.85 ± 0.34

[a] Estimated graphically, from a maximum of five data points. [b] ± refers to standard deviations. [c] Derived activation parameters, calculated for 75 °C: $\Delta H_B^‡$ 68.8 (±4.5) kJ mol^{-1}, $\Delta S_B^‡$ −58 (±14) J K^{-1} mol^{-1}, $\Delta G_B^‡$ 89.0 (±9.3) kJ mol^{-1}; r 0.998.

in sulpholane solution at 305.5 K with *m*-nitrobenzenesulphonyl chloride was 0.23 dm^3 mol^{-1} s^{-1}.[8]

Experimental

Materials.—1,3-Dichloro-2,4-dinitrobenzene[3,10] had m.p. 342—343 K (lit.,[10] 343—344 K).

2,5-*Dichloro*-3-*nitrothiophene.* Potassium nitrate (5.2 g) was added in portions with stirring to a solution of 2,5-dichlorothiophene (15.3 g) in concentrated sulphuric acid (100 ml) at 283 K. The mixture was set aside at 283 K for 30 min and then poured onto crushed ice. The oil which separated was taken up in ether, the extract washed with aqueous sodium hydrogencarbonate and water, and dried (Na_2SO_4), and the solvent removed. The residue was dissolved in light petroleum and chromatographed on a column of silica gel, with light petroleum as eluant, to give 2,5-dichloro-3,4-dinitrothiophene, m.p. 364 K,[11] and 2,5-*dichloro*-3-*nitrothiophene*, m.p. 323 K (Found: Cl, 36.0; N, 7.2. $C_4HCl_2NO_2S$ requires Cl, 35.8; N, 7.1%); δ ($CDCl_3$) 7.74 (s, H-4).

Potassium 4-chloro-3,5-dinitrobenzenesulphonate was converted[12,13] into 4-chloro-3,5-dinitrobenzenesulphonyl chloride, m.p. 372—373 K (lit.,[13] 372 K); δ ($CDCl_3$) 8.86 (s, H-2 and -6); $\lambda_{max.}$ ($CHCl_3$) 290 nm (ε 109.5 m^2 mol^{-1}).

Kinetics.—The kinetic procedures used were those described earlier: for compound (I) the method[14] involving isolation of samples of the substrate was used; for compound (II) the method[15] involving estimation of inorganic chloride as silver chloride was employed; for compound (III) the 'single-point' technique[14] was used for the fast initial points, whilst the slow reaction was followed by the normal sampling technique.

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